Analyzing & Testing

NETZSCH

Leading Thermal Analysis

NETZSCH KINETICS NEO SOFTWARE DEMONSTRATION

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Sitzung der ERFA-BCI ‚Gefährliche Reaktionen', Sisseln, 24 January 2019

Purpose of kinetic analysis

Academic

1. Activation energy for the peak point
2. Activation energy for different stages of process
3. Scientific research of the process, including information about each reaction step.

Industrial

1. Prediction at the same ranges of temperature and heating rate as in experiment (no extrapolation), based on kinetic analysis
2. Predictions at the temperatures and/or heating rates outside of the experimental range (extrapolation), based on kinetic analysis
3. Optimization of industrial processes

KINETICS NEO

- A Software for studying **chemical kinetics** (reaction kinetics) and **crystallization kinetics**.
- It investigates the **reaction rates** of chemical processes or crystallization depending on **time** and **temperature**.
- Kinetics Neo contains **10 model-free methods** including numerical methods for the best model-free results.
- Kinetics Neo features a unique **model-based method** that allows for analyzing multi-step processes, determines a kinetic model, makes predictions and optimizations based on this model.

Steps of work

- Experiment
- Analysis
- Predictions

1 Experimental data

Data for analysis: ASCII or SCV (3 columns)

TGA, DSC

- Dynamic DSC, different heating rates
- Isothemal DSC: different temperatures

Calorimetric data:

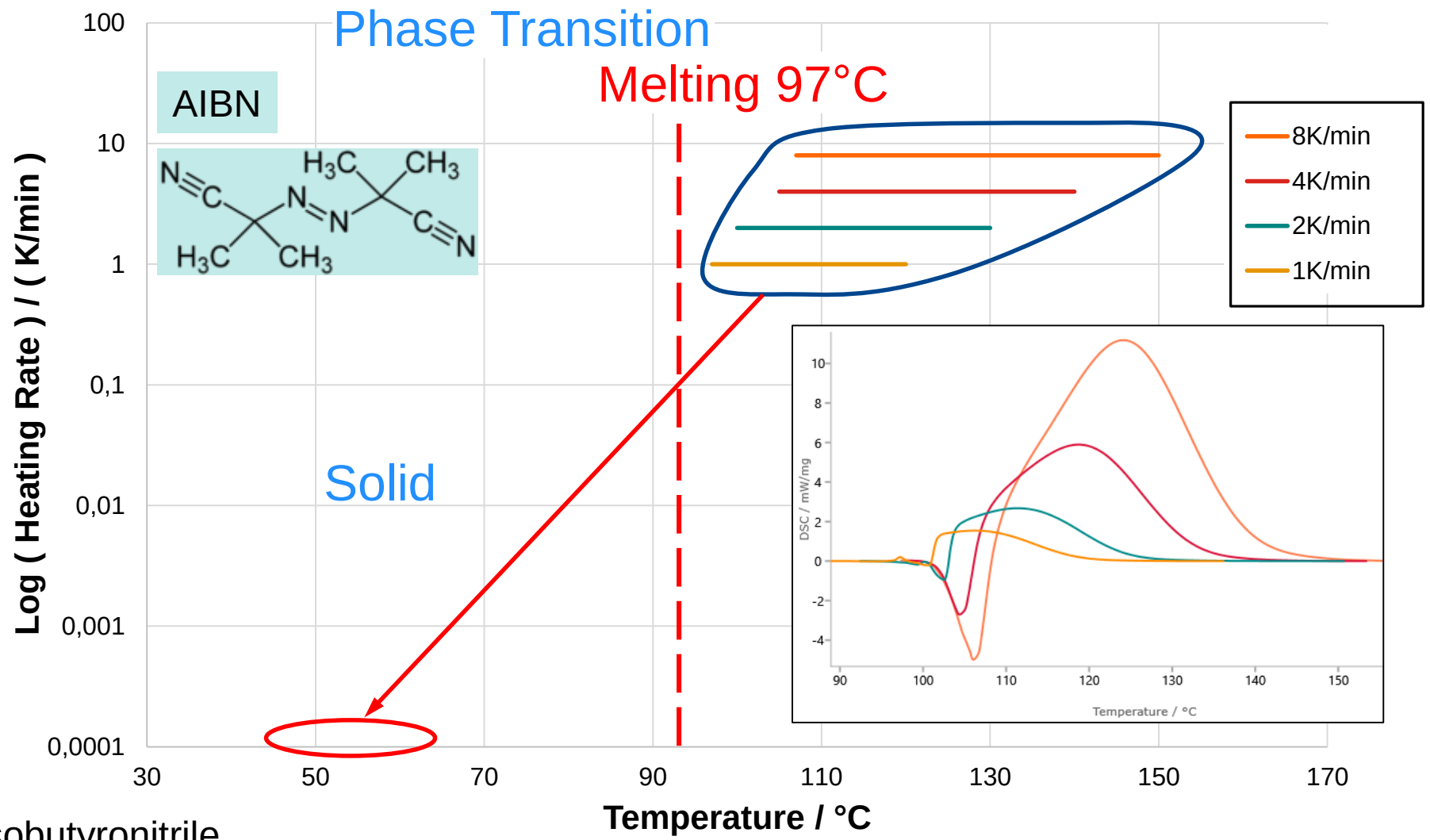
- HFC different temperatures
- ARC, APTAC, MMC

Additional

- DIL, DEA, Viscosity, Rheometry

Data can be imported from the projects of Thermokinetics3

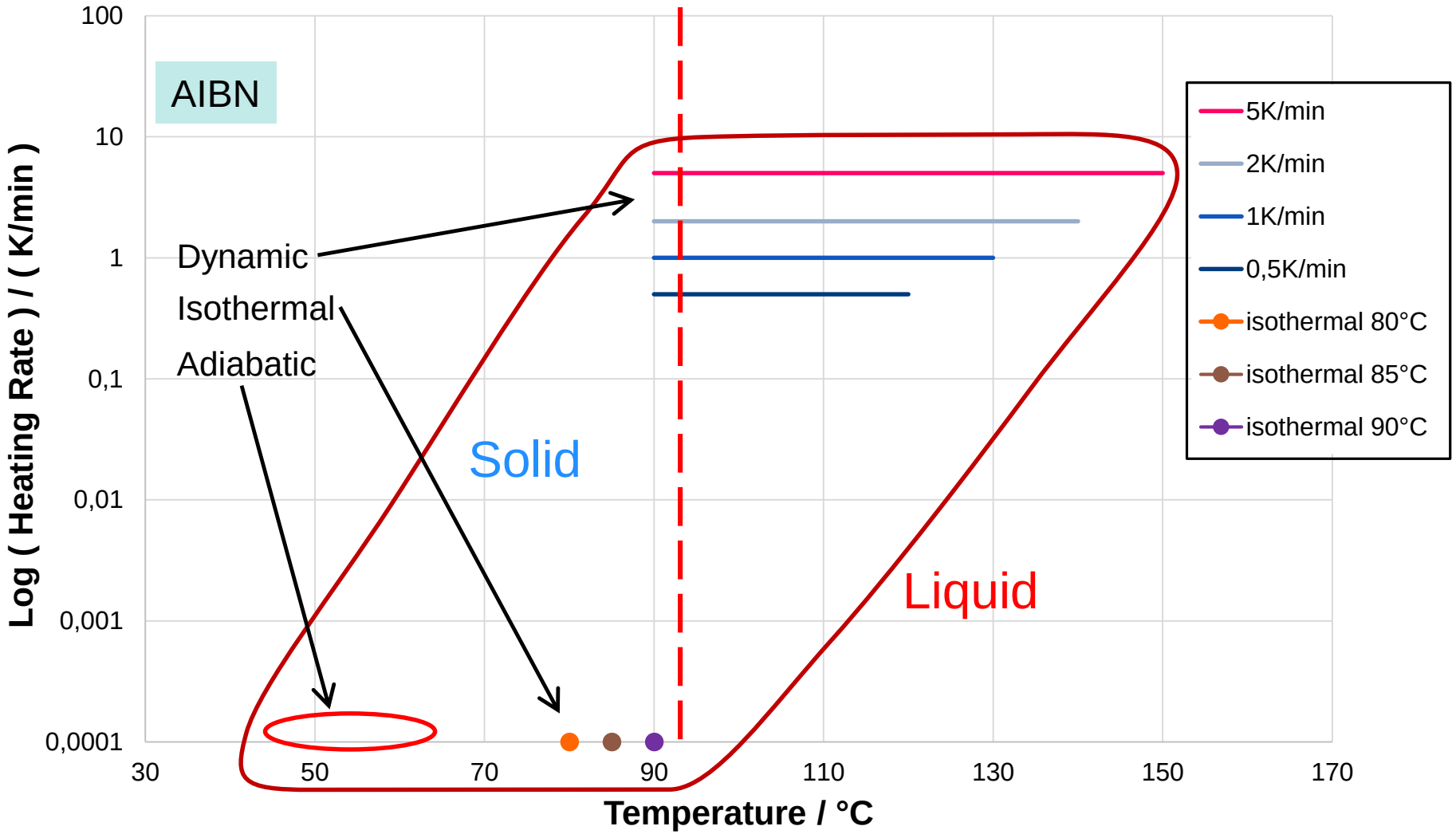
Data field depends on the target
Different temperatures – different kinetics



AIBN: Azobisisobutyronitrile

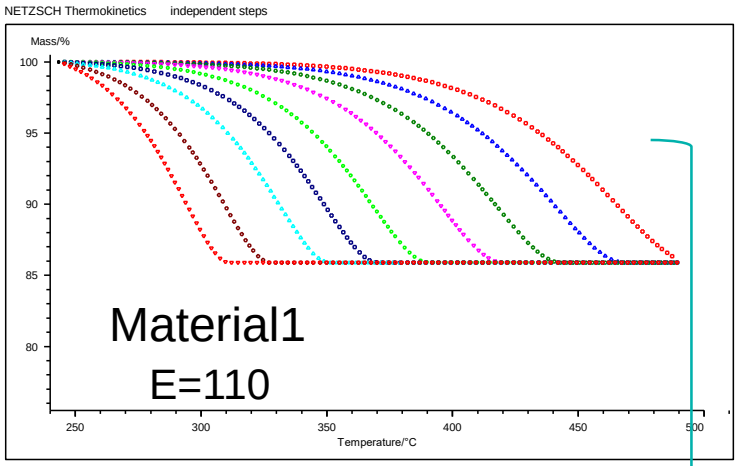
S.Guo, J.Therma Anal Calorim (2013) 113:1169-1176 SADT:63°C for 50kg (AKTS)

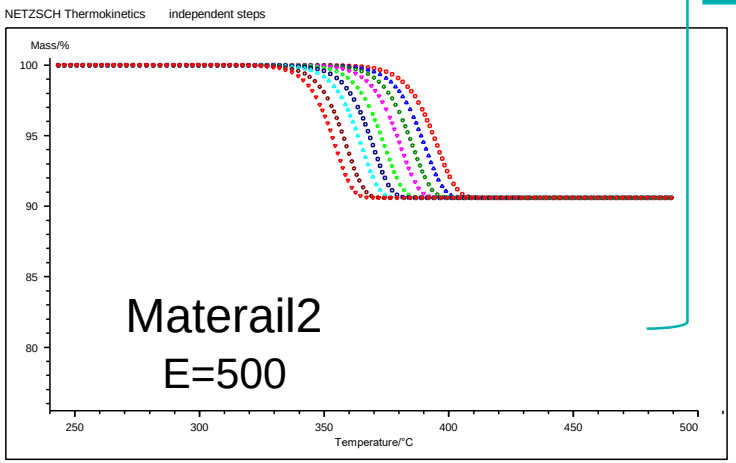
Data field depends on the target
Experiment must be done for the same state of material

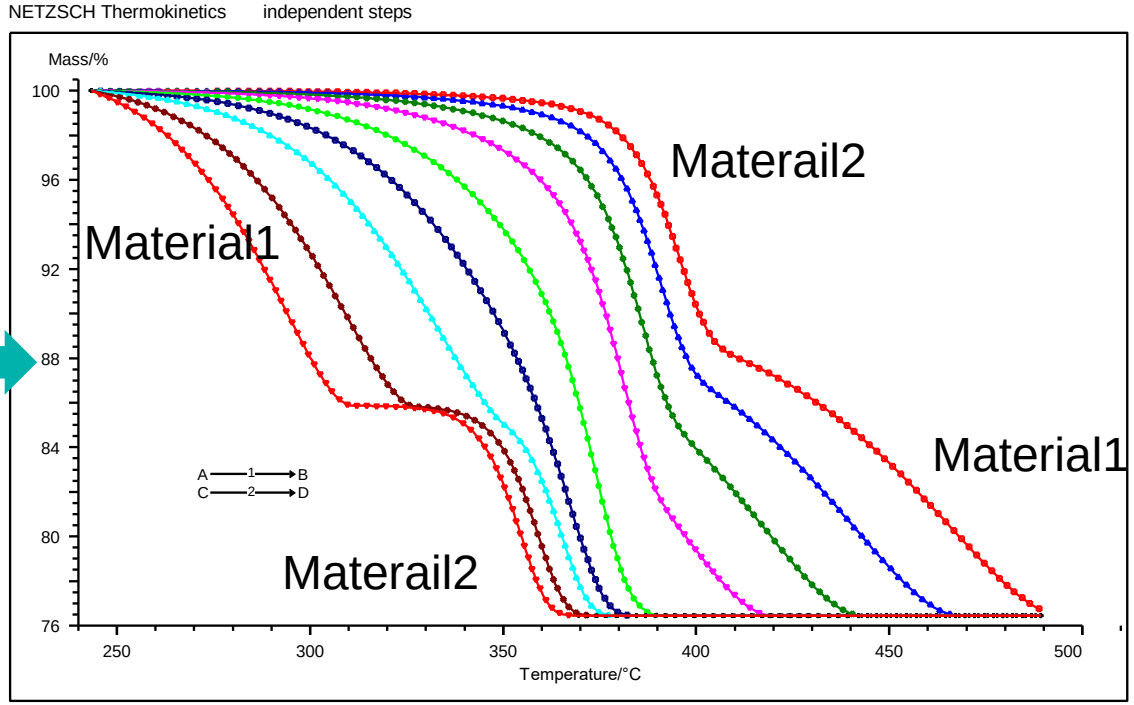


Moukhina, Thermochimica Acta 621(2015) 25-35, SADT 46°C, measurements: BAM

Different heaating rates different kinetics
Decomposition of mixtures







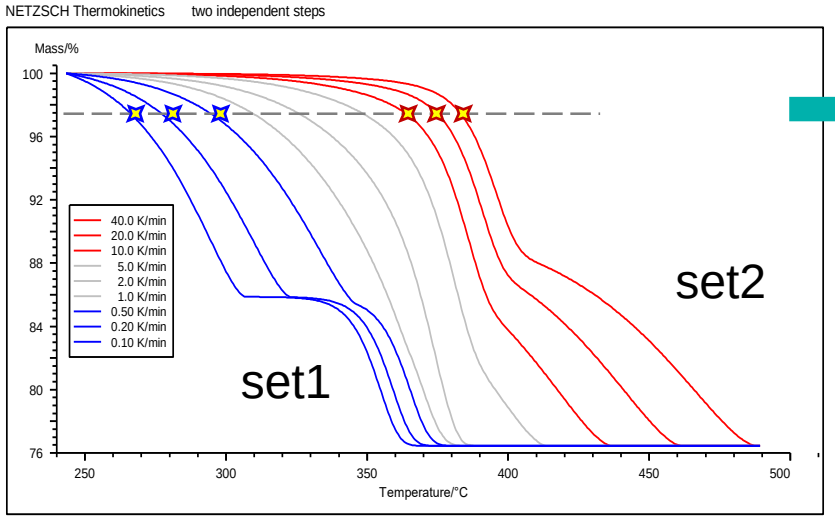
mixture

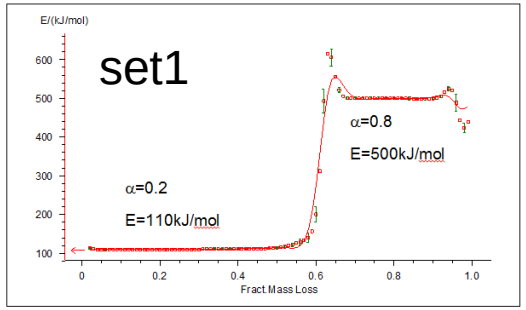
Heating Rate from 0.1K/min to 50K/min

Moukhina, J Therm Anal Calorim (2012) 109:1203–1214

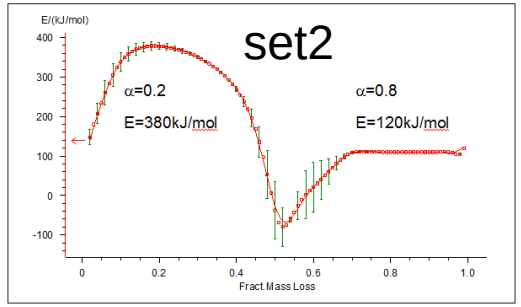
Lifetime predictions for mixture

Dynamic data: two data sets

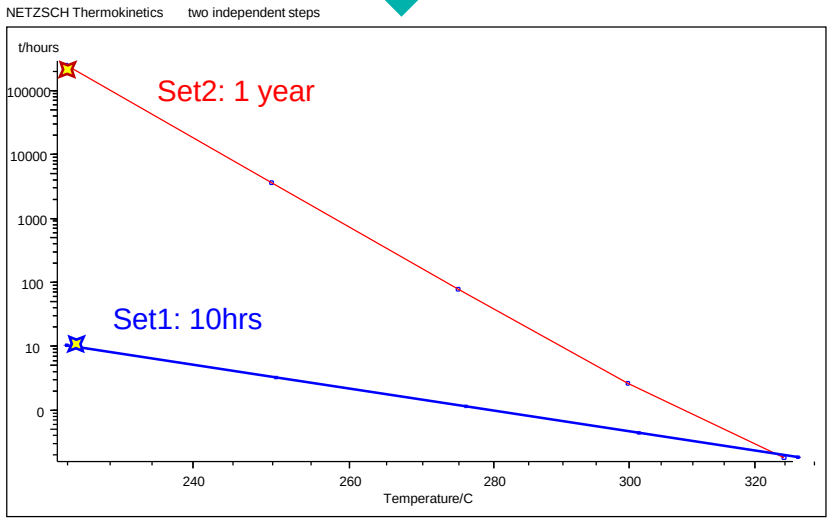




Simulation E=110, 500,
Model-free E=110,500,



Simulation E=110, 500,
Model-free E=380,120,



Lifetime predictions by model-free are different

Moukhina, ASTM Journal of Testing and evaluation (2014) V42,N6: 1376-1386

2 Analysis Method

Model-free and **model-based** methods.

The results of these methods can be statistically compared with one another.

- **Model-free**
  - activation energy and pre-exponential factor as functions of the conversion degree.
- **Model-based**
  - kinetics model including
  - Number of reaction steps
  - Step contribution to the total effect

- **Parameters for each reaction step:**
  - Reaction type
  - Activation energy
  - Reaction order

- **Parameters for crystallization:**
  - Dimension of nucleation
  - Melting temperature and glass transition temperature

Approaches:

Model-free

$A \rightarrow B$

α - conversion

$$\frac{d\alpha}{dt} = A(\alpha) \cdot f(\alpha) \cdot \exp\left(\frac{-E_A(\alpha)}{RT}\right)$$

E_A – Activation energy

f(α) – Reaction type

A – Pre-exponential factor

(in gas describes the number of particle collisions)

1. One equation for any reaction
2. Activation energy depends only on conversion
   And independent on measurement conditions
3. f(α) is assumed to be n-th order reaction

Model-based (any model)

$A \rightarrow B \rightarrow C \rightarrow \ldots$

a – concentration of A
b – concentration of B
c – concentration of C

$$\begin{cases} \frac{d\,(a \rightarrow b)}{dt} = A_1\, f_1\,(a) \exp\left(-\frac{E_{A1}}{RT}\right) \\ \frac{d\,(b \rightarrow c)}{dt} = A_2\, f_2\,(b) \exp\left(-\frac{E_{A2}}{RT}\right) \\ \ldots \end{cases}$$

1. Reaction has several steps
2. Reaction steps can be parallel or consecutive
3. Each reaction step has own kinetic equation
4. Kinetic parameters of each step are constant values

Conversion-dependent methods

• Ozawa-Flynn-Wall	Integral isoconversional method for each conversion point	heating
• Kissinger-Akahira-Sunose	Integral isoconversional method for each conversion point	heating
• Friedman method	differential isoconversional method for each conversion point	heating+iso
• Numerical optimization	modified Friedman method	
	to get minimum of $\psi = \sum_{curves} \sum_{points} \left(\alpha_i^{calc} - \alpha_i^{exp}\right)^2$	heating+iso

Methods based on the single conversion

• ASTM E698	integral Ozawa method for points with Maximum rate	heating
• ASTM E2890	integral Kissinger Method for points with maximum rate	heating
• ASTM E1641	integral Ozawa method for points with 5% conversion	heating
• ASTM E2070	Integral isoconversional method for isothermal data	isothermal
• Dynamic Arrhenius	integral Ozawa method for failure temperature at heating	heating
• Isothermal Arrhenius	integral isoconversional method for time-to-event (e.g. OIT)	isothermal

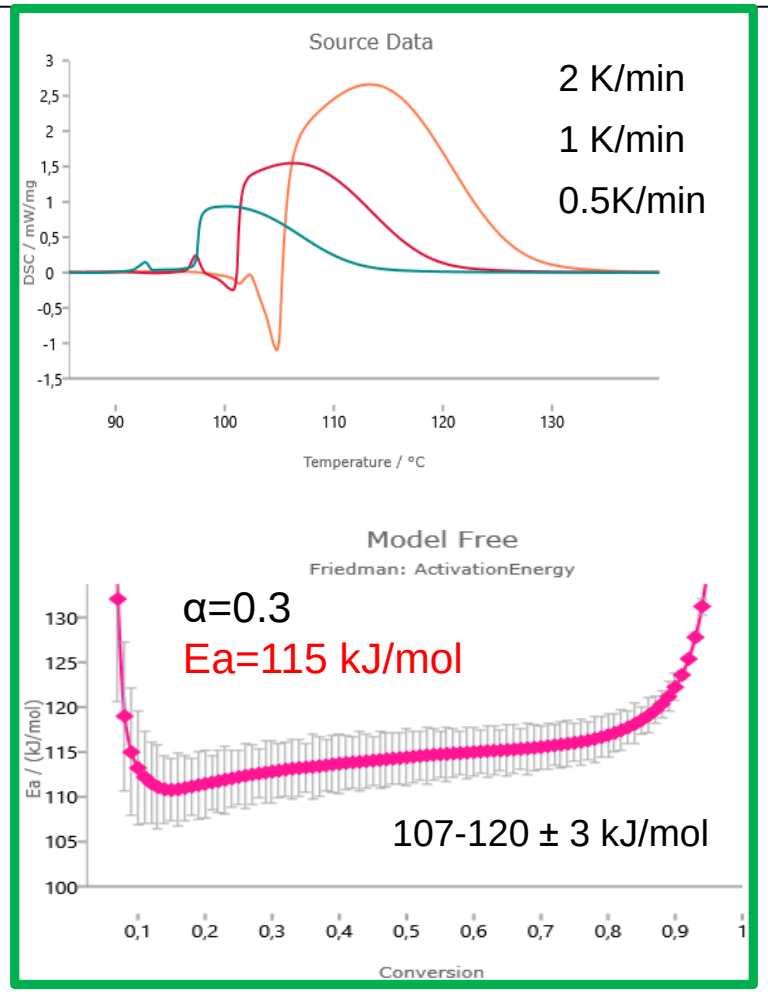
Select the analysis method

1. No scientific research, no predictions:
   ASTM, Friedman, Ozawa, Kissinger, model based for 1-2steps

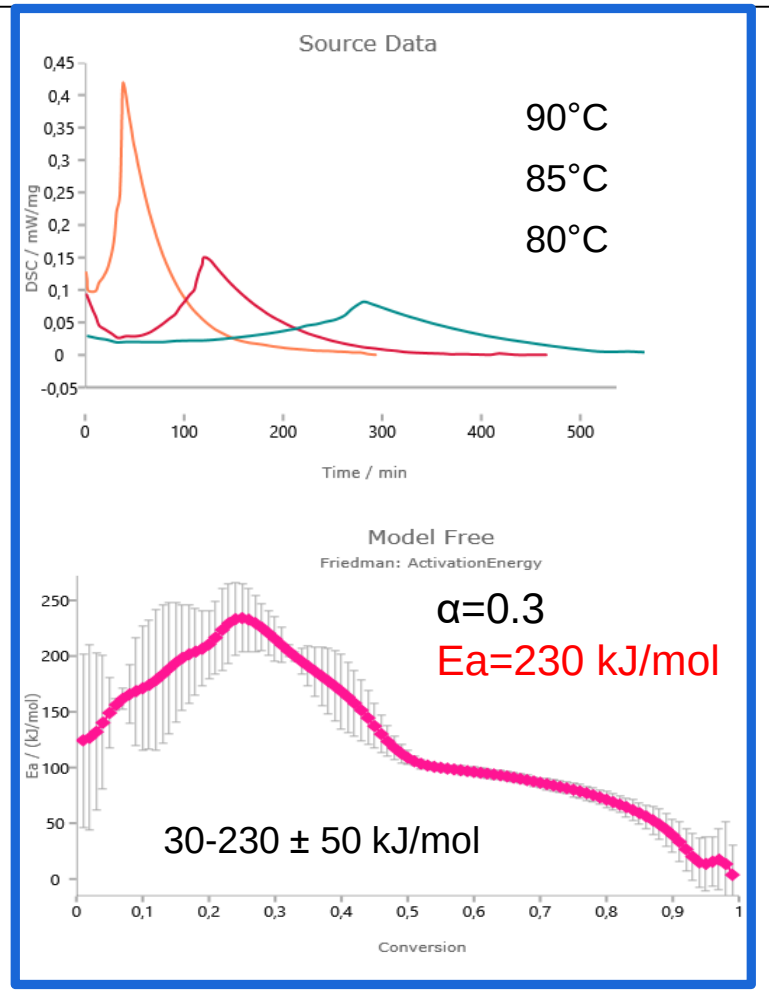
2. Deep scientific research: both model free and model based
   Model free: Friedman or numerical methods produce best fit
   Model based: allow to find parallel steps: independent or competitive

3. Predictions with extrapolation on heating rate:
   Model free, if it has the same result for isothermal and dynamic data
   Model based, if isoconversional lines have crossing by decreasing of HR

Why and when model free analysis is inapplicable?
Example: model free analysis for dynamic and isothermal data is not the same



Dynamic

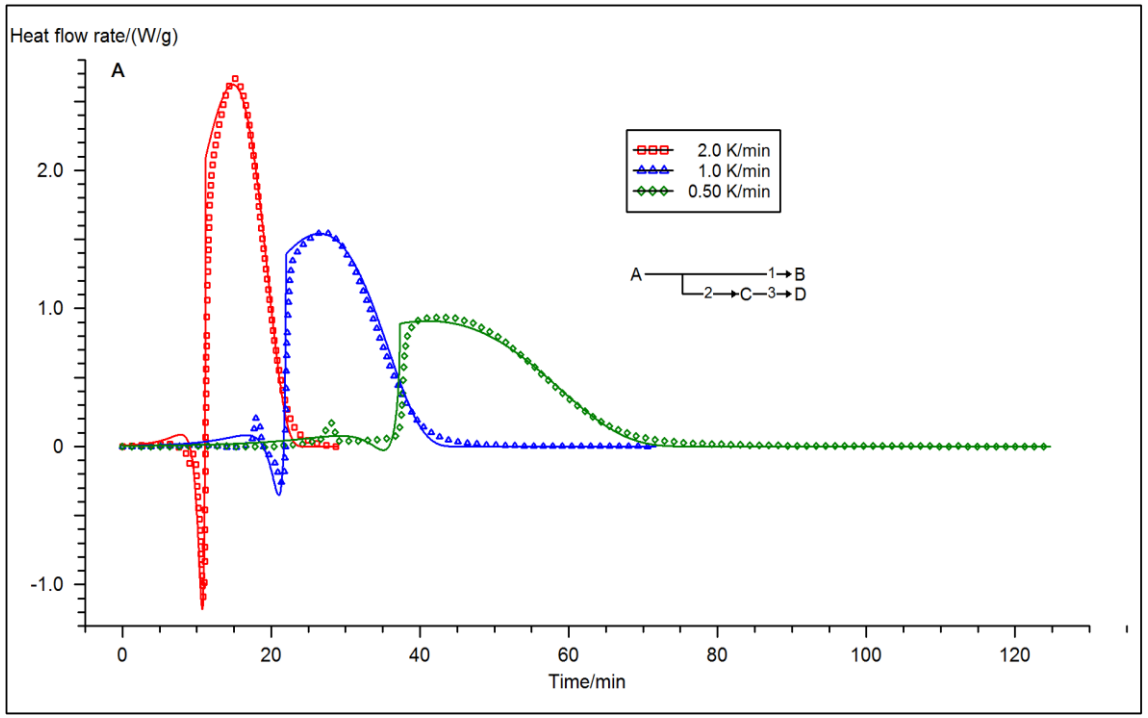


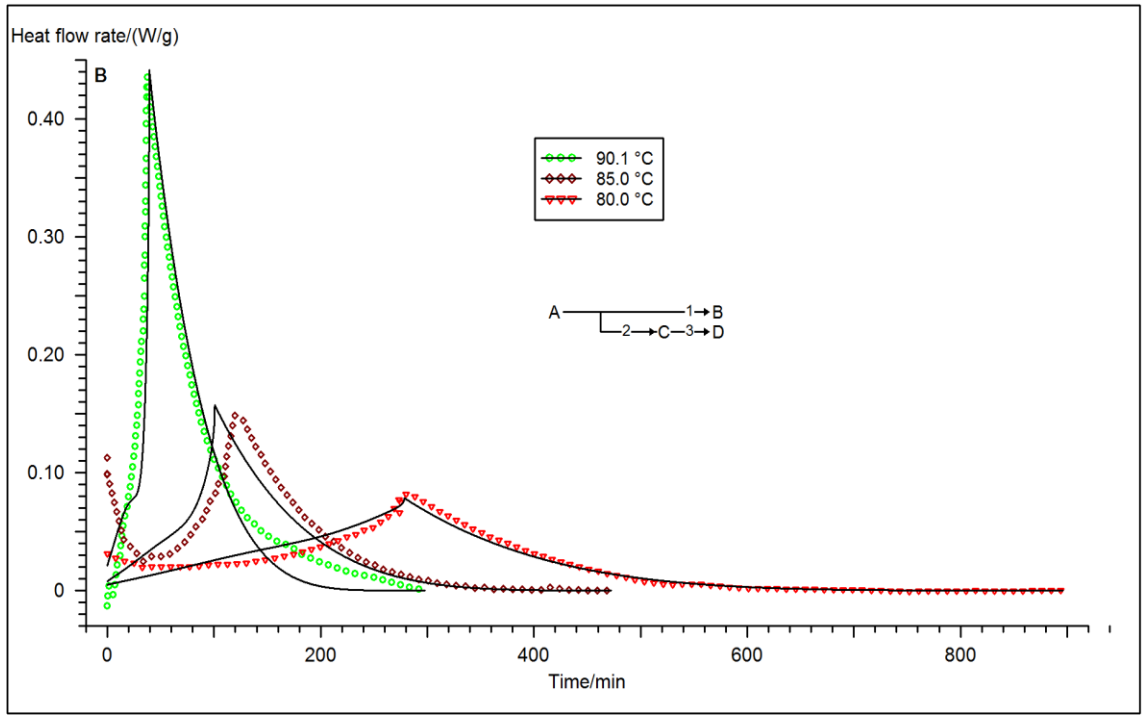
Isothermal

AIBN: different results for different Heating Rates

Moukhina,Thermochimica Acta 621(2015) 25-35

Model-based analysis: AIBN

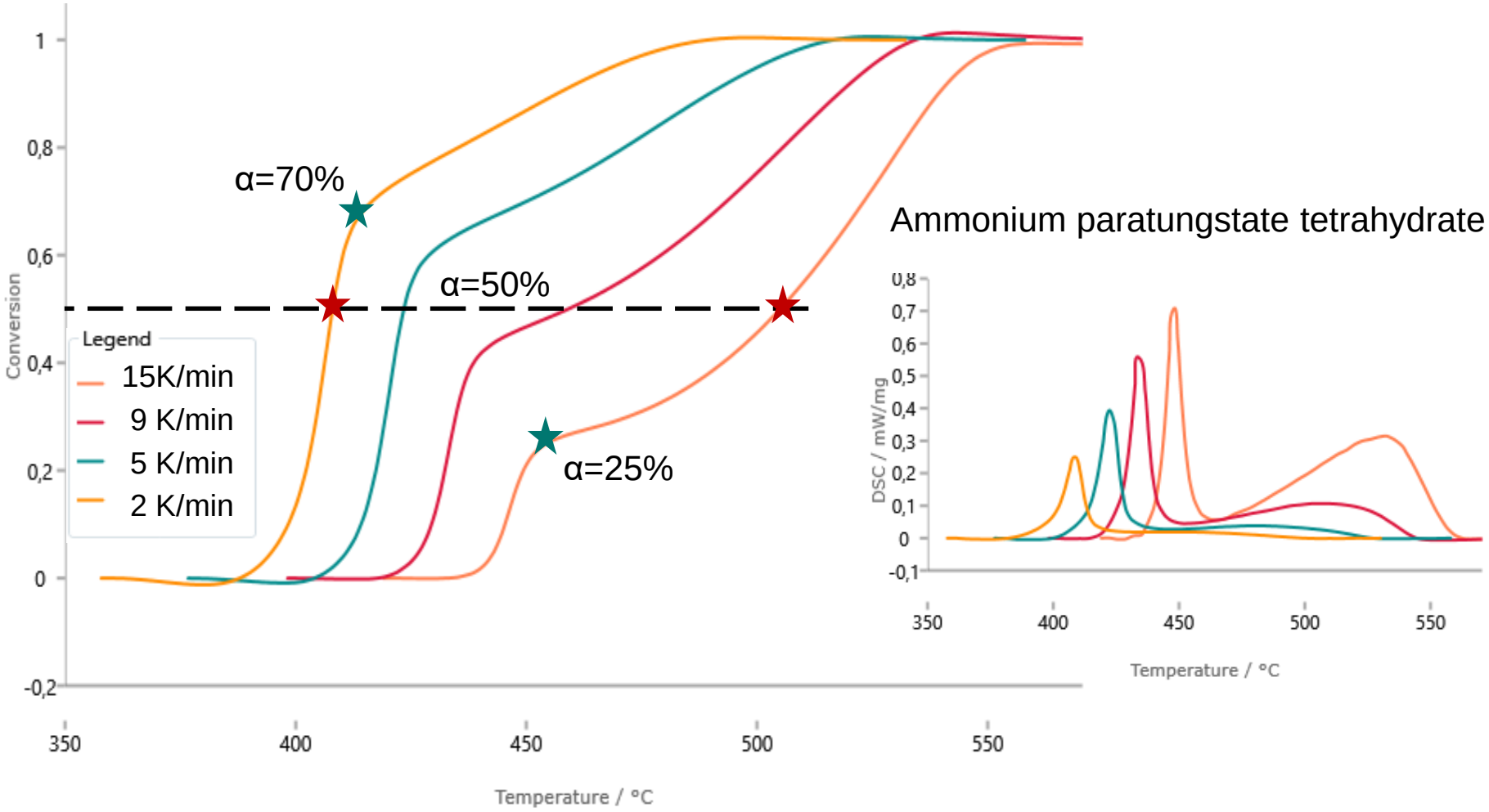




Decomposition of Azobisisobutyronitrile (AIBN)

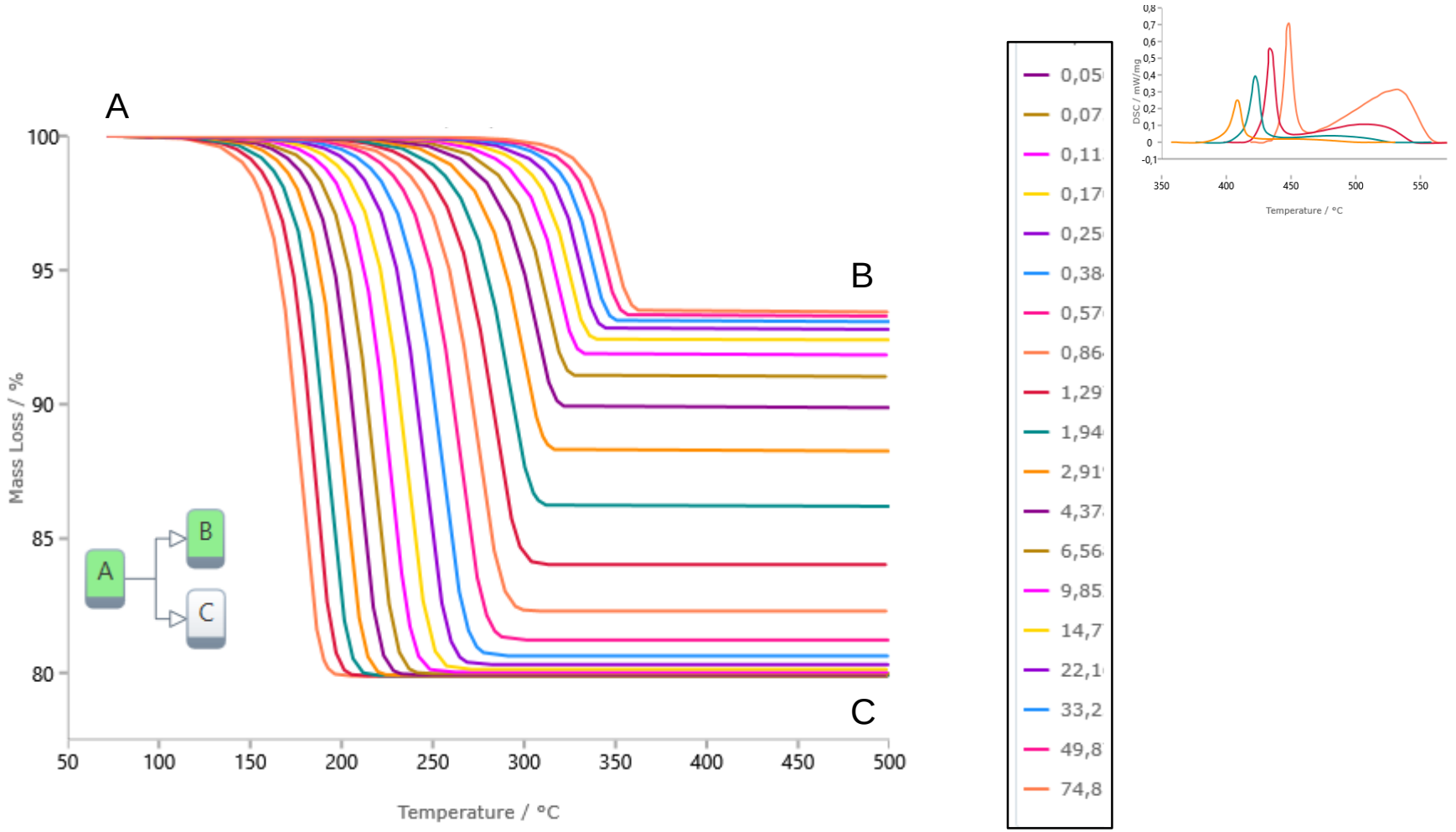
Moukhina, Thermochimica Acta 621(2015) 25-35

When model-free methods do not work?
Example: kinetic mechanism changes at different conversion



Data from Fait, Moukhina, Thermochimica Acta, 637 (2016) 38-50

When model-free methods do not work?
Example: competitive steps

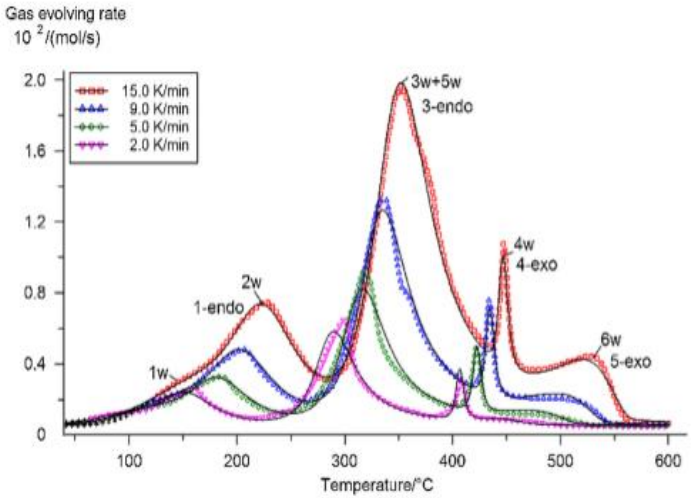


Total effect depends on the heating rate

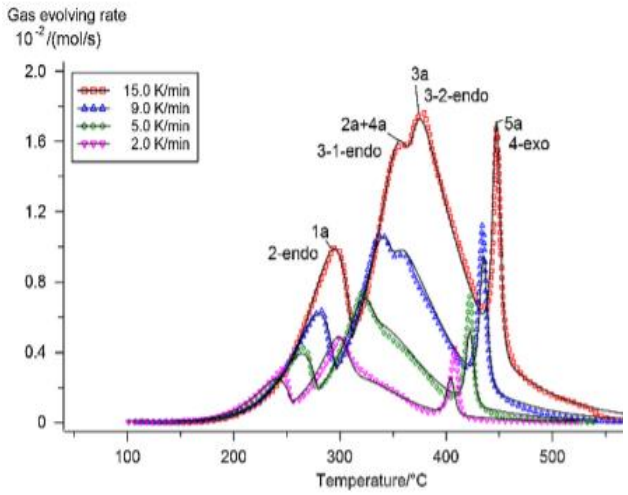
Kinetics Neo: Model based analysis

- Modelling
  - unlimited number of models
  - unlimited number of reaction steps
  - individual steps are linked as independent, parallel, competing or following
  - Visual creation of a kinetic model
  - Visual adding, removing or editing of each reaction step.
  - Visual adjustment of position and contribution of each step.
  - Optimization of kinetic parameters for one individual step.
  - Optimization of kinetic parameters for the complete kinetic model.
- Reaction types
  - Reaction of 1st, 2nd and n-th order without autocatalysis
  - Reaction of 1st, 2nd and n-th order with autocatalysis including Prout-Tompkins and Kamal-Sourour reactions
  - 2-/3-dim. phase boundary reactions
  - 1-/2-/3-dim. diffusion (Jander's type and Ginstling-Brounstein)
  - 2-/3-/n-dim. nucleation according to Avrami
  - Curing Reactions with diffusion control (using Di Benedetto model or splines for dependence Tg vs Alpha)
  - Crystallization according to the Nakamura equation using the Hoffman-Lauritzen Theory

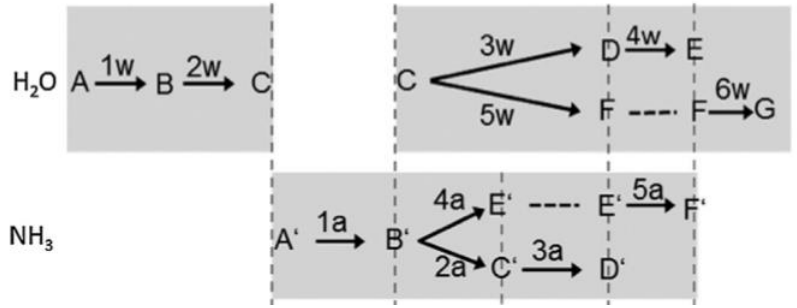
Model-based analysis:
Ammonium paratungstrate tetrahydrate, MS decomposition curves

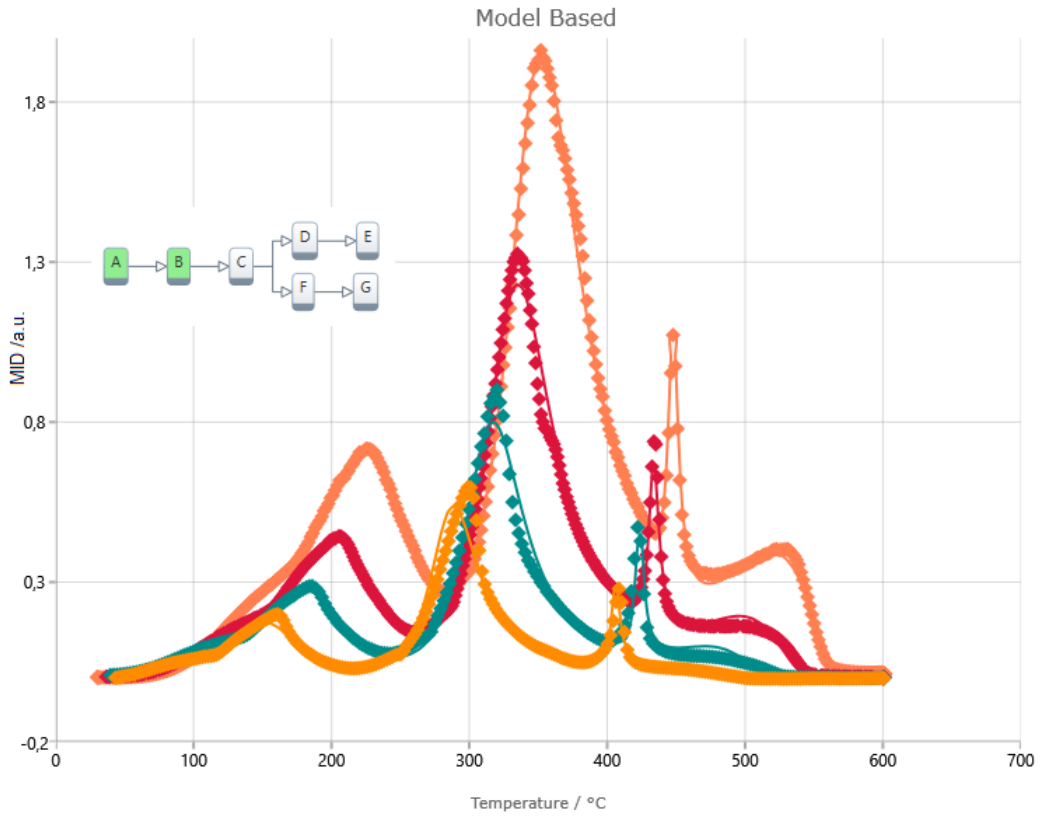


MS curves for water



MS curves for ammonia





M.J.G. Fait, Elena Moukhina, et al. Thermochimica Acta 637 (2016) 38–50

3 Predictions

Predictions

• Isothermal predictions	Predictions for several isothermal temperatures
• Isothermal lifetime predictions	Predictions for given conversion at several isothermal temperatures
• Dynamic prediction	Predicitons for several heating rates for reactions or for several cooling rates for crystallization
• Multi-step prediction	Prediction for a user-defined sequence of dynamic and isothermal segments with the possibility of export/import of multi-step program to/from text file
• Step-iso prediction	Prediction of a step-iso temperature program, respesenting a stepwise temperature increase
• Modulated predictions	Prediction of a modulated temperature program which is the sum of an underlying constant temperature or constant heating and a sinus-shaped temperature oscillation
• Adiabatic prediction	Calculation of the adiabatic temperature increase for various initial temperatures.
• TTT diagram	Time-Temperature-Transition diagram for reactions with diffusion control.

Results of prediction

- Measurement output (signal)
- Conversion
- Conversion rate
- Concentration for each reactant (model-based)
- Reaction rate for each reaction step (model-based)

The simulated values can be presented:

- Curves as a function of time or temperature
- Table with simulated values, time and temperature